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④ PROCESS FOR PRODUCING QUARTZ GLASS.

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**Description****Technical field**

This invention is related to a silica glass formation process, and more particularly to a silica glass formation process at a low temperature by the sol-gel technology using a metal alkoxide as raw material.

**Background art**

Silica glass has been recognized to be very advantageous for many uses, such as crucibles, boards and quartz tubes of furnaces in the manufacturing process of semiconductors, since it has been possible to 10 prepare a silica glass of high purity. Besides, silica glass is used for a glass equipment such as a beaker for chemistry and a cell for optical measurement. Further, the development of the silica glass having less hydroxyl groups or having good optical uniformity permits the various optical uses of silica glass. Especially, attention is given to silica glass fiber for optical communication. Furthermore, silica glass is used for a substrate of a Thin Film Transistor. In this way, silica glass is widely applied in various fields and 15 the demand thereof is expected to increase still more in future.

At present, silica glass is mainly obtained by the following three approaches.

**Method (1) wherein;**

Cleanly refined native quartz is washed and melted.

20 **Method (2) wherein;**  
 $\text{SiO}_2$  is formed from raw material  $\text{SiCl}_4$  or  $\text{SiH}_4$  of high purity.

**Method (3) wherein;**

25 a native silica sand is melted.  
 Whichever method is used, however, prepared silica glass is expensive due to the high temperature treatment which is inevitably included in the manufacturing process and the difficulty in manufacturing glasses on their own.

Accordingly, more economical processes are desired for preparing silica glass. In order to prepare 30 silica glass cheaply, two approaches are practiced; one is a sol-gel technology wherein a metal alkoxide is used as raw material, the other is a sol-gel technology wherein fumed silica is used as raw material. Each approach is described hereinafter.

The sol-gel process for economically preparing silica glass from metal alkoxides is studied by Nogami and Moriya, in *Journal of Non-Crystalline Solids*, 37, (1980) pp. 191-201.

35 The steps of this process are as follows; Silicon alkoxide, water, alcohol and proper catalyst such as hydrochloric acid or ammonia are mixed together and hydrolyzed. After gelling the hydrolyzed solution, the gel is dried to form dry gel. Dry gel is sintered by increasing temperature and collapsed completely to form silica glass. According to this sol-gel process, silica glass allowed to be highly pure for an alkoxide used as raw material is easily purified. In addition, manufacturing cost is less expensive than the 40 conventional process for heat treatment is carried out at low temperature.

On the contrary, this process suffers the deficiency that large articles of dry gel tend to crack during 45 drying and similarly during heating in a process of conversion from dry gel to silica glass. Under the condition, the obtained silica glass is not sufficiently large to put into practical use. So far as known from references, a disc type silica glass of 28 mmφ obtained by the study of Nogami and Moriya seems to be the largest at present.

On the other hand, the sol-gel process in which fumed silica is used as raw material is disclosed in 50 *Journal of Non-crystalline solids*, 47, (1982) pp. 435-439 by E. M. Rabinovich et al. Fumed silica (trademark: Cab-o-sil supplied by Cabot Corp.) is mixed with water to be a hydrosol. After the hydrosol is gelled, the gel is dried to form dry gel, which is converted to silica glass by sintering. Being different from said metal alkoxide process, this sol-gel process using fumed silica has an advantage that the dry gel is hard to be broken or cracked during drying and sintering, which permits the formation of fairly large silica glass. Nevertheless, a realized silica glass in the aforesaid reference is at most as large as 95×15×5 mm 55 (including a 4%  $\text{B}_2\text{O}_3$ ), which appears to be maximum in size. Moreover, this sol-gel method is disadvantageous in that the bubbles are so easily generated that there is a lot of cells in a realized silica glass. Therefore, this sol-gel process is unsuitable for an application requiring an optical uniformity.

As mentioned above, the conventional sol-gel process has not been enough sufficient to be applied in various field, since prepared silica glass thereby is neither so large nor so good in quality.

**60 Disclosure of invention**

The object of this invention is to provide an improved process for forming a silica glass plate of large size or a silica glass mass of large volume at low cost as compared to the conventional, with using a new sol-gel technology.

Another object of this invention is to provide an improved process for forming a silica glass of high 65 quality.

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A further object of this invention is to provide an improved process for forming a silica glass in good yield.

The process of the invention is defined in claim 1. Claims 2—21 recite improvements of the process. In a preferred embodiment, the process comprises:

- 5     hydrolyzing a solution of ethyl silicate;
- casting the solution by pouring into a container of desired shape, sealing the container and permitting it to stand at room temperature to gel;
- replacing the cover of the container with a lid formed with apertures comprising between 0.5 to 20% of the surface area of the lid;
- 10    drying the gel in the container to form a dry gel by heating to 60°C at a heating rate of 2°C per hour and drying for 7 days;
- heating the dry gel to 200°C at a heating rate of 60°C per hour and maintaining the dry gel at 200°C for one hour to remove absorbed water;
- heating the dry gel at a heating rate of 180°C per hour to 950°C and maintaining that temperature for 18
- 15    hours to remove carbon and ammonium chloride; and
- heating the dried gel to 1200°C at a heating rate of 180°C per hour and maintaining the temperature at 1200°C for 1.5 hour to yield the silica glass, characterized in that it comprises after the step of hydrolyzing and before the step of casting
- adding fumed silica or silica gel powder to the solution in an amount from 0.2 to 5 mols of fumed silica
- 20    or silica gel powder per mol of ethyl silicate;
- adjusting the pH to between 4.0 and 4.5 by addition of ammonia to the solution.

In the invention, a metal alkoxide is hydrolyzed to be a sol solution. The silica is added in the sol solution with stirring. After the stirred solution is gelled, the gel is dried to be dry gel. A silica glass is formed by heating the dry gel until it becomes non-porous. A summary of the invention is described hereinafter.

Water and hydrochloric acid, or proper solvent if need be, are added into the silicon alkoxide and hydrolyzed to be sol. The silica (white carbon such as trademark: Aerosil supplied by Deutsche Gold & Silber Scheideanstalt Vormals Roessler Co., trademark: Cabo-o-Sil supplied by Cabot Co., trademark: D. C. Silica supplied by Dow Corning Co., trademark: Arc Silica supplied by PPG Industries Inc., and so on) are added to the sol with well stirring. The sol is casted into the container of hydrophobic material such as polypropylene, polyvinylchloride, polyethylenefluorid (trademark: Teflon) and glass. The casted sol is gelled and dried to be dry gel. Dry gel is slowly heated from room temperature to a predetermined temperature where dry gel is kept until the pores therein are completely collapsed, in resulting to form a silica glass. Nogami et al's research tells that the way for preventing the dry gel from cracking during sintering in the sol-gel technology using a metal alkoxide as raw material is to form a porous dry gel including a great quantity of large pores of about 50 to 100 Å in diameter. A forming process of a silica glass according to this invention will be further described hereinafter. This is also supposed by that E. M. Ravinovich et al's dry gel obtained by sol-gel technology using a fumed silica as raw material is hard to crack during sintering, and that the dry gel synthesized by hydrolyzing a metal alkoxide with ammonia

40    (which is rather porous than the dry gel materialized by hydrolyzing a metal alkoxide with acid) is hard to crack during sintering. Further, the research of the inventors proves that the hardness of uncrackable dry gel against an intensive shrinkage during drying is determined by the pH value of the sol solution. Namely, the sol solution in which a metal alkoxide is hydrolyzed using an acid as catalyst indicates 1—2 pH value. As the pH value of the sol is higher, the synthesized dry gel is hard to crack, in resulting to be large dry gel.

45    In the light of the above, this invention has a feature that the silica is added into a sol solution including a hydrolyzed metal alkoxide. The advantages brought by addition of the silica is that a dry gel becomes so porous as to hardly crack during sintering, and that the pH value of the sol increases to about 2—3 so that the gelling speed is increased and the gel becomes hardly crackable during drying. Thus, this invention allows appearance of a large silica glass which has not been obtained by the conventional sol-gel method. 50    In addition, the silica glass obtained by the forming process according to this invention has an optically good quality with remaining no cell therein during sintering.

A silica obtained by wet process using sodium silicate as a raw material may be substituted for the white carbon obtained by hydrolyzing  $SiCl_4$  with an oxyhydrogen flame burner, such as trademark Aerosil and Cab-o-sil, discharges the duties, since a silica has only to be effective in making the dry gel porous. It is well known that silica fine particles are produced by hydrolyzing metal alkoxide with ammonia. A silica similar to the white carbon is produced by salvage of silica fine particles. Adding of this salvaged silica into a sol has the same effect as adding of the white carbon.

Next, the conditions for improving the yield of dry gel based on the research of inventors will be described. The container of hydrophobic material, where the gel is cast, is good for drying gel. This is because the dry gel shrinks to 70% of the original in length during drying, so that the gel must easily slide in the container with weak affinity therebetween. Organic polymer such as polypropylene, polyvinylchloride, polyethylenefluorid, polyethylene and polystyrene is suitable for a material of the container. The container of inorganic material whereon the organic material is coated has the same effect as the container of organic material.

65    With reference to drying condition, the evaporating speed of solvent in the gel such as water and

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alcohol is effective. The optimum drying condition must be set up in due consideration of the ratio of the area of the penetration holes in the lid of the container wherein the gel is cast to the total area of the lid (hereinafter referred to as the aperture rate), the drying temperature and the humidity.

Reduction in evaporating speed of the solvent in the gel with small evaporating rate contributes to 5 make the gel uncrackable. However, as it takes many days to manufacture the dry gel, the manufacturing cost amounts to expensive. Consequently, it is desired to make yield good in short manufacturing time. Drying temperature influences the toughness of the gel. The higher the temperature is, the much tough gel is. As a result, good yield is taken. However, the temperature beyond boiling point of the solvent is so high that the evaporating speed can not be controlled. The maximum of the temperature is about 120°C. Thus, it 10 has been found in the experiment that the gel should be cast in the container with a lid of aperture rate less than 50%, preferably less than or equal to 10%, and dried at less than 120°C.

Furthermore, the sol cast in the container should be gelled at as low a temperature as possible for the purpose of preventing generation of bubbles therein. Normally, bubbles are apt to generate in the sol or in the surface where the sol and the container are connected. However, the lower the gelation temperature is, 15 the less the bubbles generate. When the temperature at this time (hereinafter referred to as gelling temperature) is beyond 60°C, the bubbles generate in the almost all sol. After sintering, these bubbles remain in the silica glass and optical quality is deteriorated. On the other hand, when the gelling temperature is too low, gelling speed drops and the manufacturing costs become too expensive. The minimum temperature is 5°C to keep the practical gelling speed. The practical gelling temperature should 20 be between 5°C and 60°C. After gelation is completed, a heating rate from gelling temperature to drying temperature should be low in order to obtain good yield, while it should be high in order to decrease the manufacturing time. The maximum temperature of heating rate is practically 120°C/h. A maximum dry gel of 12 cmφ is obtained under the above mentioned conditions.

It is aforementioned that the pH value of the sol is increased from 1—2 to 2—3 by adding the silica in 25 resulting that the tough gel can be obtained which is uncrackable against the intensive shrinkage during drying. Therefore, a further large dry gel is obtained by increasing the pH value with addition of a base such as ammonia. As a result of the experiments, it is proved that the most tough and most uncrackable gel is obtained with pH value of 3—6. Thus, in a forming process of silica glass according to this invention, a further large silica glass can be obtained with adjustment of pH value of the sol. The following materials are 30 suitable for bases of adjusting pH value; ammonia, ammonia gas, a solution of ammonia or an organic base, especially triethylamine, a solution of triethylamine, pyridine or a solution of triethylamine, aniline, or a solution of aniline. On the contrary, an inorganic base including metal alkaline ion such as sodium hydride and potassium hydride is unsuitable for forming a silica glass since cation remains in the silica glass whereby the composition of the silica glass is changed. The inorganic base is suitable for 35 multi-component glasses such as a soda glass.

Next, conditions for sintering to obtain a silica glass of high quality in a good yield will be described hereinafter. Sintering comprises the following three processes;

- (1) process of removing the absorbed water
- (2) process of removing carbon
- 40 (3) process of making gel non-porous.

Process (1) has influence on the yield at sintering. Dry gel involves a large amount of physically absorbed water to be removed at 400°C. At the heat treatment, abrupt rise of temperature for taking the absorbed water makes dry gel crackable easily, in resulting poor yield. Therefore, the heating rate should be low in order to make the yield good. While, the heating rate should be high in considering the 45 manufacturing cost. The maximum of the heating rate is 400°C/h so far as the yield is reasonable. Further, heat treatment should include at least one process of maintaining the gel for 1 hour or more at a predetermined temperature between 20°C (a room temperature) and 400°C.

Process (2) is carried out at 400°C—1100°C. The heating rate during this heat treatment has an influence on the yield, even though not so much as process (1). The experiments by the inventors prove that 50 appropriate heating rate is between 30°C/h and 400°C/h. Further, heat treatment should desirably include one process of maintaining the gel for 3 hours or more at a predetermined temperature between 400°C and 1100°C. At the time when the pH value is adjusted, basic-acid reaction matter remains in a dry gel. To be effective, this basic-acid reaction matter is decomposed during the process of removing carbon. It is desirable to lengthen the maintaining time in this case.

Process (3) is carried out at 1000°C to 1400°C, which is a little depending on the adding amount of the 55 silica. The most suitable heating rate from process (2) to process (3) is between 30°C/h and 400°C/h. A transparent silica glass having the same near infrared spectrum, Vickers hardness, a bulk density and the like as those of the silica glass on the market are formed by maintaining a dry gel for a predetermined time at a temperature where pores are collapsed. In this case, a dry gel is maintained for a long time at the 60 temperature exceeding the above after pores are completely collapsed, bubbles are apt to generate. Generation of bubbles is due to the water remaining in a silica glass after collapsing pores. The less amount of water a silica glass includes, the less bubbles generate. Water content in a silica glass is a function of the adding amount of the silica. With increasing adding amount of the silica, the involved water is so decreased that bubbles hardly generate. Therefore, a large amount of adding the silica is favorable for preventing 65 generation of bubbles. On the contrary, the yield of dry gel at drying comes poor with a large amount of

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adding the silica. In order to hardly generate bubbles with good yield, the silica should be added so that the metal alkoxide and the silica may be in the ratio mol of 1:0.2—5.

On the other hand, there is a case where crystal such as cristobalite and tridymite is generated in a silica glass after sintering. This is a sort of devitrification. It has been found that a non-homogeneous dispersion of the silica in sol and/or a very small amount of impurities cause devitrification. To use the ultrasonic wave vibration and the centrifugal separation is effective for improving dispersion. Especially, small amount of impurities are removed by the centrifugal separation, whereby preventing occurrence of devitrification.

As described above, this invention can provide the large silica glass of about 15×15 cm which have been unprecedented by the conventional sol-gel method. Further, this invention can provide a silica glass in more than 90% yield with much lower cost than the conventional.

Furthermore, a multicomponent glass such as borosilicate glass, soda glass, silica/alumina glass, alkali-proof glass of  $\text{SiO}_2-\text{SrO}_2$  group, and low-expansion coefficient glass of  $\text{SiO}_2-\text{TiO}_2$  group are allowed to be manufactured with low cost by applying this invention.

This invention is of great advantage to expansion of the demand of the silica glass in the field wherein the silica glass is applied. Furthermore, it is also of great advantage to expansion of new demand in the field wherein the silica glass has not been allowed to be applied due to the high cost.

### Brief description of drawing

Fig. 1 illustrates the near infrared spectra of the silica glass obtained by the process in accordance with this invention and the silica glass obtained by the melting process on the market.

### Best mode of carrying out the invention

#### Example 1

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 72 g (1.2 mol) of fumed silica (trademark: Cab-o-sil, whose surface area is 200 m<sup>2</sup>/g supplied by Cabot Corp.) was added to the solution with stirring. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 2% and the casting was heated from 20°C to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 19 cm×19 cm×0.6 cm which was uncrackable at room temperature (20°C). In the experiment, the sol prepared as described above was cast into 20 similar container and dried in the same condition. Then 2 out of 20 gels cracked and 18 were perfect, showing that the yield was 90%.

Thus prepared 18 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 1 hour to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1200°C at a heating rate of 180°C/h and maintaining at 1200°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 18 samples in the 100%.

The near infrared spectra of the silica glass prepared in accordance with the above process (indicated by 1) and the silica glass on the market (by Sinetsu Sekiei Co., Ltd.) prepared by the melting process (indicated by 2) are shown in Fig. 1. As can be seen in Fig. 1, they have almost the same near infrared spectrum of the silica glass. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 792 and thermal expansion coefficient of  $5.4 \times 10^{-7}$ . Therefore, the silica glass of this example is regarded to be the same material as the fused silica glass.

#### Example 2

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 25.8 g (0.43 mol) of fumed silica (trademark: Nipsil E220A which is obtained by wet process with sodium silicate as raw material supplied by Japan Sekiei Industry Corp., diameter of particle is 1.5 μm) was added to the solution with stirring and ultrasonic vibration was applied. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 0.8% and the casting was heated from 20°C to 70°C at a heating rate of 2°C/h. The gel was dried at 70°C for 12 days to yield a hard dry gel as large as 18 cm×18 cm×0.6 cm which was uncrackable at room temperature. In the similar containers

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and dried in the same condition. Then 3 out of 20 gels cracked and 17 were perfect, showing that the yield was 85%.

Thus prepared 17 dry gels were heated from room temperature to 300°C at a heating rate of 60°C/h and maintained at 300°C for 2 hours to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1120°C at a heating rate of 180°C/h and maintaining at 1120°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. In the sintering process as above, 2 out of 17 samples cracked in 88.2% yield.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.18, Vickers hardness of 790 and thermal expansion coefficient of  $5.4 \times 10^{-7}$ .

### Example 3

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. Mixture of 14 ml of 28% ammonia, 10 l of ethanol and 200 ml of water was added to the solution of 800 ml of ethylsilicate and 3.4 l of ethanol and stirred at room temperature. The stirred mixture was left overnight and then a powder of silica is salvaged under reduced pressure. Then, the powder silica is left to stand 200°C under air of nitrogen all the night. 60 g (1 mol) of powder of silica obtained in this way was added into the hydrolyzed solution with stirring and ultrasonic vibration was applied to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 1% and the casting was heated from 20°C to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 3 out of 20 gels cracked and 17 were perfect, showing that the yield was 85%.

Thus prepared 17 dry gels were heated by sintering from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours and further heated to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. The sintering process as above caused cracking of 5 to 17 samples and 12 perfect gels were obtained in a 70.6% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality. The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.21, Vickers hardness of 811 and thermal expansion coefficient of  $5.6 \times 10^{-7}$ .

### Example 4

280 ml of 0.01 mol/l hydrochloric acid was added to 152 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 90 g (1.5 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration applied. Massive matter was removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ammonia thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 0.8% and the casting was heated from 20°C to 70°C at a heating rate of 5°C/h. The gel was dried at 70°C for 7 days to yield a hard dry gel as large as 20 cm×20 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then none of 20 gels cracked, showing that the yield was 100%.

Thus prepared 20 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours. The samples then were heated to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. These gels were further heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1230°C at a heating rate of 180°C/h and maintaining at 1230°C for 1 hour, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were

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obtained. The sintering process as above did not cause cracking of any one of 20 samples in a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process 5 presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.19, Vickers hardness of 771 and thermal expansion coefficient of  $5.8 \times 10^{-7}$ .

### Example 5

10 280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 73 g (1.22 mol) of fumed silica (Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dripping 15 0.1 mol/l ethanol solution of triethylamine thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 40°C and gelled in 10 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 1% and the casting was heated 20 from 40°C to 70°C at a heating rate of 5°C/h. The gel was dried at 70°C for 7 days to yield a hard dry gel as large as 18.5 cm × 18.5 cm × 0.65 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same way. Then 2 out of 20 gels cracked and 18 were perfect, showing that the yield was 90%.

25 Thus prepared 18 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours, and further heated to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 900°C at a heating rate of 180°C/h and maintained at 900°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm × 15 cm × 0.5 cm were obtained. The 30 sintering process as above did not cause cracking of any one of 18 samples in a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process 35 presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 790 and thermal expansion coefficient of  $5.6 \times 10^{-7}$ .

### Example 6

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available 40 ethylsilicate with violently stirring and the material was hydrolyzed. 73 g (1.22 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ethanol solution of pyridine thereto. The sol was cast as thick as 1 cm 45 into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 5°C. Then the cover of the container was replaced by a lid with aperture rate 1% of the total area of the lid and the casting was heated from 5°C to 60°C at a heating rate of 5°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 18.8 cm × 18.8 cm × 0.65 cm which was uncrackable at room temperature. In the 50 experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 3 out of 20 gels cracked and 17 were perfect, showing that the yield was 85%.

Thus prepared 17 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours. The dry gels were further heated from 200°C to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 900°C at a heating rate of 180°C/h and maintained at 900°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm × 15 cm × 0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 17 samples in a 100% yield.

The near infrared spectrum of the silica glass prepared in accordance with the above process 60 presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 760 and thermal expansion coefficient of  $5.6 \times 10^{-7}$ .

### Example 7

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available 65 ethylsilicate with violently stirring and the material was hydrolyzed. 60 g (1 mol) of fumed silica (trademark:

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Cab-o-sil, whose surface area is 200 m<sup>2</sup>/g supplied by Cabot Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of more perfect uniformity. The pH of the resultant sol was adjusted to 4.5 by making the diluent gas of ammonia gas with nitrogen gas bubble therein. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 30°C and gelled in 30 minutes. Then the cover of the container was replaced by a lid with aperture rate 5% and the casting was heated from 30°C to 60°C at a heating rate of 5°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 5 out of 20 gels cracked and 15 were perfect, showing that the yield was 75%.

Thus prepared 15 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours. Dry gel was further heated to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 19 samples in a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.19, Vickers hardness of 790 and thermal expansion coefficient of 5.4×10<sup>-7</sup>.

### 25 Example 8

180 ml of 0.02 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 100 g of water and 60 g (1 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied to obtain a sol of more perfect uniformity. The pH of this sol was 2.15. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 16 cm, the length of 16 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 0.1% and the casting was heated from 20°C to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 15 days to yield a hard dry gel as large as 11.5 cm×11.5 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 8 out of 20 gels cracked and 12 were perfect, showing that the yield was 60%.

Thus prepared 12 dry gels were heated by sintering from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours. The gels were further heated to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 3 hours to remove carbon and ammonium chloride. After further heating to 1200°C at a heating rate of 180°C/h and maintaining at 1200°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 8 cm×8 cm×0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 12 samples in a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides, the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.21, Vickers hardness of 790 and thermal expansion coefficient of 5.6×10<sup>-7</sup>.

### Example 9

180 ml of 0.02 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 100 ml of water and 73 g (1.22 mol) of fumed silica (trademark: Aerosil 0×50, whose surface area is 50 m/g supplied by Aerosil Corp.) were added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of more perfect uniformity. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 1% and the casting was heated from 20°C to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol

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prepared as described above was cast into 20 similar containers and dried in the same condition. Then 1 out of 20 gels cracked and 19 were perfect, showing that the yield was 95%.

Thus prepared 19 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours. The dry gels were further heated to 300°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 19 samples in a 100% yield.

Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 800 and thermal expansion coefficient of  $5.5 \times 10^{-7}$ .

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### Example 10

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 300 g (5 mol) of fumed silica (Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.0 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 25°C and gelled in 50 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 2% and the casting was heated from room temperature to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition.

30

Then 5 out of 20 gels cracked and 15 were perfect, showing that the yield was 75%.

Thus prepared 15 dry gels were heated from room temperature to 300°C at a heating rate of 10°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 600°C at a heating rate of 320°C/h and maintained at 600°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1400°C at a heating rate of 320°C/h and maintaining at 1400°C for 0.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 15 samples in a 100% yield. Moreover, all of the obtained silica glasses were free from bubbles in spite of high temperature treatment at 1400°C.

40 The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.18, Vickers hardness of 760 and thermal expansion coefficient of  $5.8 \times 10^{-7}$ .

### Example 11

180 ml of 0.02 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 100 ml of water and 12 g (0.2 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) were added to the solution with stirring and ultrasonic vibration was applied to yield a sol of better uniformity. The pH of the resultant sol was adjusted to 3.0 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 5°C overnight.

50 Then the cover of the container was replaced by a lid with aperture rate 0.8% and the casting was heated from 5°C to 60°C at a heating rate of 2°C/h. The casting was dried at 60°C for 10 days to yield a hard dry gel as large as 18.0 cm×18.0 cm×0.6 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 10 out of 20 gels cracked and 10 were perfect, showing that the yield was 50%.

60 Thus prepared 10 dry gels were heated from room temperature to 200°C at a heating rate of 10°C/h and maintained at 200°C for 3 hours. Next, the samples were heated to 300°C at a heating rate of 10°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 600°C at a heating rate of 20°C/h and maintained at 600°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1000°C at a heating rate of 30°C/h and maintaining at 1000°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 14.0 cm×14.0 cm×0.45 cm were obtained. During the sintering process as above, 3 out of 10 samples cracked in 70% yield. Moreover, the

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obtained silica glasses were free from bubbles even if maintained for 30 minutes at 1200°C, while bubbles generated at 1300°C.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.19, Vickers hardness of 780 and thermal expansion coefficient of  $5.6 \times 10^{-7}$ .

### Example 12

280 ml of 0.01 mol/l hydrochloric acid was added to 152 g (1 mol) of purified commercially available methoxidesilicate with violently stirring and the material was hydrolyzed. 90 g (1.5 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) were added to the solution with stirring and ultrasonic vibration was applied to yield a sol of better uniformity. The pH of the resultant sol was adjusted to 6.0 by dripping 0.1 normal ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 5°C and gelled in 10 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 2% and the casting was heated from 5°C to 65°C at a heating rate of 5°C/h. The casting was dried at 65°C for 7 days to yield a hard dry gel as large as 18.5 cm × 18.5 cm × 0.63 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 20 dry gels were obtained, showing that the yield was 100%.

Thus prepared 20 dry gels were heated from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 3 hours. Next, the samples were heated to 300°C at a heating rate of 400°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 1000°C at a heating rate of 400°C/h and maintained at 1000°C for 8 hours to remove carbon and ammonium chloride. After further heating to 1150°C at a heating rate of 400°C/h and maintaining at 1150°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 14.5 cm × 14.5 cm × 0.5 cm were obtained. During the sintering process as above, 2 out of 20 samples cracked and 18 were perfect in a 90% yield. Moreover, all of the obtained silica glasses were free from bubbles even if maintained for 30 minutes at 1200°C, while bubbles generated at 1300°C.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.19, Vickers hardness of 780 and thermal expansion coefficient of  $5.6 \times 10^{-7}$ .

### Example 13

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 75 g (1.22 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.5 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of Teflon® having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at room temperature and gelled in 50 minutes.

Further the gelled casting was maintained overnight. Then the cover of the container was replaced by a lid with aperture rate 2% and the casting was heated from room temperature to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as large as 21 cm × 21 cm × 0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 20 perfect dry gels were obtained, showing that the yield was 100%.

Thus prepared 20 dry gels were heated from room temperature to 300°C at a heating rate of 180°C/h and maintained at 300°C for 1 hour to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 320°C/h and maintained at 950°C for 18 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 320°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm × 15 cm × 0.5 cm were obtained. During the sintering process as above, 1 out of the 20 samples cracked in 95% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 800 and thermal expansion coefficient of  $5.4 \times 10^{-7}$ .

### Example 14

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 120 g (2 mol) of fumed silica

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(trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.3 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a 5 cubical container of glass whose surface was coated with polyvinyl chloride having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 20°C and gelled in 30 minutes. Further the gelled casting was maintained overnight.

Then the cover of the container was replaced by a lid with aperture rate 2% and the casting was heated from 20°C to 60°C at a heating rate of 2°C/h. The gel was dried at 60°C for 7 days to yield a hard dry gel as 10 large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar molds and dried in the same condition. Then 1 out of 20 gels cracked and 19 were perfect in 95% yield. Thus prepared 19 dry gels were heated by sintering from room temperature to 200°C at a heating rate of 60°C/h and maintained at 200°C for 1 hour to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 15 950°C for 9 hours to remove carbon and ammonium chloride. After further heating to 1280°C at a heating rate of 180°C/h and maintaining at 1280°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. During the sintering process as above, 1 out of the 18 samples cracked in 94.7% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

20 The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 805 and thermal expansion coefficient of 5.5×10<sup>-7</sup>.

### 25 Example 15

280 ml of 0.01 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 73 g (1.22 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the 30 solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 4.1 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of glass whose surface was coated with polyvinyl chloride having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 60°C and gelled in 10 minutes. Then the cover of the container was replaced by a lid with 35 a hole whose area was 0.5% of the total area of the lid and the casting was heated from 60°C to 120°C at a heating rate of 2°C/h. The gel was dried at 120°C for 4 days to yield a hard dry gel as large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 6 out of 20 gels cracked and 14 were perfect in 70% yield.

40 Thus prepared 14 dry gels were heated from room temperature to 400°C at a heating rate of 60°C/h and maintained at 300°C for 5 hours to remove the absorbed water. The samples then were heated to 1100°C at a heating rate of 180°C/h and maintained at 1100°C for 3 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the 45 samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. During the sintering process as above, 3 out of the 14 samples cracked in 78.6% yield. The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.2, Vickers hardness of 800 and thermal expansion coefficient of 5.5×10<sup>-7</sup>.

### 50 Example 16

280 ml of 0.05 mol/l hydrochloric acid was added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 73 g (1.22 mol) of fumed silica (trademark: Aerosil OX50, whose surface area is 50 m<sup>2</sup>/g supplied by Aerosil Corp.) was added to the 55 solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The pH of the resultant sol was adjusted to 5.0 by dripping 0.1 mol/l ammonia solution thereto. The sol was cast as thick as 1 cm into a cubical container of polypropylene having the width of 30 cm, the length of 30 cm and the height of 10 cm and the container was sealed. The casting was permitted to stand at the temperature of 5°C overnight. Then 60 the cover of the container was replaced by a lid with aperture rate 50% the casting was heated from 5°C to 20°C at a heating rate of 120°C/h. The gel was dried at 20°C for 22 days to yield a hard dry gel as large as 21 cm×21 cm×0.7 cm which was uncrackable at room temperature. In the experiment, the sol prepared as described above was cast into 20 similar containers and dried in the same condition. Then 16 out of 20 gels cracked and 4 were perfect, showing that the yield was 20%.

65 Thus prepared 4 dry gels were heated from room temperature to 200°C at a heating rate of 10°C/h and

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maintained at 200°C for 2 hours. Next, the samples were heated to 300°C at a heating rate of 10°C/h and maintained at 300°C for 2 hours to remove the absorbed water. The samples then were heated to 950°C at a heating rate of 180°C/h and maintained at 950°C for 6 hours to remove carbon and ammonium chloride. After further heating to 1220°C at a heating rate of 180°C/h and maintaining at 1220°C for 1.5 hours, the samples became non-porous and the transparent silica glasses as large as 15 cm×15 cm×0.5 cm were obtained. The sintering process as above did not cause cracking of any one of 15 samples in a 100% yield. Moreover, all of the obtained silica glasses were free of either devitrification or bubbles and proved to be of high-quality.

The near infrared spectrum of the silica glass prepared in accordance with the above process presented almost the same shape as that of the silica glass now on the market. Besides the near infrared spectrum, the silica glass of this example has the same properties as the silica glass on the market, such as bulk density of 2.19, Vickers hardness of 810 and thermal expansion coefficient of  $5.4 \times 10^{-7}$ .

### Example 17

15 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified ethylsilicate on the market. The mixture was stirred for 30 minutes sufficiently to conclude the hydrolysis. The 40 g of fumed silica trademark: Cab-o-sil was added to the hydrolyzed mixture with stirring. After ultrasonic vibration is applied for homogenizing the solution for 30 minutes, the large lump of Cab-o-sil or some foreign particles were filtered to be more homogenized. 0.1 mol/l ammonia solution was dropped in 20 the homogenized sol to adjust the pH of solution to 4.4. The sol was cast as thick as 1 cm into the container of polypropylene (23 cm in inside diameter) and maintained. The casting was gelled in 30 minutes. Further the casting was maintained for 10 days at room temperature, in resulting that white dry gel of 15 cm was obtained with shrinkage of the gel. Subsequently the dry gel was heated to 1150°C at a heating rate of 180°C/h, so that the dry gel becomes transparent. As a result, a silica glass of 10.2 cmφ was obtained.

25 The silica glass obtained in this example has bulk density of 2.2, Vickers hardness of 800 and almost the same near infrared spectrum as the silica glass on the market.

### Example 18

30 Similarly to example 17, 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 50 ml of water and 60 g of fumed silica trademark: Cab-o-sil were added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The sol was gelled under the same condition as example 17. The dry gel was sintered at 1200°C and then the silica glass of 3 cmφ was obtained.

35 The silica glass thus obtained has the same properties as the silica glass on the market similarly to example 17.

### Example 19

40 Similarly to example 18, 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 400 ml of water and 140 g of fumed silica Cab-o-sil were added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The sol was gelled under the same condition as example 18 and dried. The dry gel was sintered, so that the silica glass of 10.3 cm was obtained.

45 The silica glass thus obtained has the same properties as the silica glass on the market.

### Example 20

50 Similarly to example 18, 180 ml of 0.1 mol/l hydrochloride and 20 ml of ethanol were added to 208 g (1 mol) of purified commercially available ethylsilicate with violently stirring and the material was hydrolyzed. 800 ml of water and 240 g of fumed silica Cab-o-sil were added to the solution with stirring and ultrasonic vibration was applied. Massive matters were removed from the solution by centrifugal separation to obtain a sol of better uniformity. The sol was gelled under the same condition as example 18 and dried. The dry gel was sintered, so that the silica glass of 10.3 cmφ was obtained.

The silica glass thus obtained has the same properties as the silica glass on the market.

### 55 Example 21

1800 ml of 0.1 mol/l hydrochloride was added to 2080 g (10 mol) of purified ethylsilicate on the market. The mixture was stirred for 30 minutes sufficiently to conclude the hydrolysis, to which 1000 ml of water was added. Then 750 g of fumed silica trademark: Cab-o-sil was added to the hydrolyzed mixture with stirring. After ultrasonic vibration is applied for homogenizing the solution for 30 minutes, the large lump of Cab-o-sil or some foreign particles were filtered to be more homogenized. 0.1 mol/l ammonia solution was dropped in the homogenized sol to adjust the pH of solution to 4.4. The sol was cast as thick as 1 cm into the container of polypropylene (23 cm in inside diameter). Then the sol in the cast was put to a test to examine how long the time is required for forming a silica glass and how the yield is varied under the same conditions (the aperture rate of a lid of the container and the drying temperature) as indicated in Table 1.

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Table 1 proves that there is the maximum of the aperture rate of the lid for getting 100% yield with proper drying temperature. Namely, the aperture rate must be less than 10% at the drying temperature of 30°C. Transparent silica glass is gained by sintering any of thus obtained dry gel.

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TABLE 1

|    | Drying temperature (°C) | Aperture rate (%) | Maintainence day | Yield (%) |
|----|-------------------------|-------------------|------------------|-----------|
| 10 | 70                      | 2                 | 6                | 100       |
|    | 60                      | 5                 | 4                | 20        |
|    | 60                      | 4                 | 5                | 80        |
| 15 | 60                      | 2                 | 6                | 100       |
|    | 60                      | 1                 | 8                | 100       |
| 20 | 50                      | 5                 | 4                | 40        |
|    | 50                      | 4                 | 6                | 90        |
|    | 50                      | 3                 | 7                | 100       |
| 25 | 50                      | 2                 | 7                | 100       |
|    | 50                      | 1                 | 8                | 100       |
|    | 40                      | 10                | 6                | 20        |
| 30 | 40                      | 7                 | 8                | 100       |
|    | 40                      | 5                 | 10               | 100       |
|    | 30                      | 12                | 8                | 70        |
| 35 | 30                      | 10                | 10               | 100       |

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### Example 22

The sol obtained by the same process as the example 21 was cast into the container having a lid of a predetermined aperture rate (first aperture rate) and maintained for a predetermined days at a room temperature to be shrinkaged. Then the casting with the same lid or with an alternated lid of the different aperture rate (second aperture rate) was heated to the predetermined temperature and maintained for the predetermined days to be dry gel. The yield at the time was examined under the conditions as shown in Table 2.

45 Table 2 teaches that the dry gel can be formed in a 100% yield by being once shrinkaged at properly low temperature and subsequently be heated to high temperature, even if the aperture rate was large. Simultaneously, the days need for forming the dry gel can be decreased.

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TABLE 2

| 5  | First aperture rate (%) | Maintenance days | Second aperture rate (%) | Drying temperature (°C) | Drying days | Yield (%) |
|----|-------------------------|------------------|--------------------------|-------------------------|-------------|-----------|
| 10 | 20                      | 6                | 20                       | 80                      | 2           | 80        |
| 15 | 15                      | 6                | 15                       | 90                      | 2           | 90        |
| 20 | 10                      | 7                | 10                       | 90                      | 2           | 90        |
| 25 | 20                      | 2                | 2                        | 70                      | 4           | 90        |
| 30 | 15                      | 1                | 2                        | 70                      | 6           | 100       |
| 35 | 10                      | 1                | 2                        | 80                      | 5           | 100       |
| 40 | 5                       | 1                | 3                        | 80                      | 4           | 90        |
| 45 | 3                       | 1                | 3                        | 80                      | 4           | 100       |

## 25 Example 23

The sol obtained by the same process as the example 21 was dried to make the white dry gel of 15.0 cm by the conventional method. As shown in Table 3, the dry gel was heated from room temperature to a first maintenance temperature at a heating rate 180°C/h and maintained for a first maintenance time at the first maintenance temperature. Subsequently, the gel was heated to a second maintenance temperature at a heating rate of 180°C/h and maintained for a second maintenance time at the second maintenance temperature. Similarly the gel was further heated to a third maintenance temperature and maintained for the third maintenance time. Then, the gel was similarly heated to 1150°C and maintained for 3 hours, and the silica glass was prepared by sintering.

It is proved that the silica glass obtained in this example are free from bubbles even if heated for 30 minutes at 1300°C. In a case where the sum total of maintenance time is equal, the longer the maintenance time at high temperature is, the less bubbles generate.

TABLE 3

| 40 | First maintenance |          | Second maintenance |          | Third maintenance |          |
|----|-------------------|----------|--------------------|----------|-------------------|----------|
|    | temperature (°C)  | time (h) | temperature (°C)   | time (h) | temperature (°C)  | time (h) |
| 45 | 950               | 18       | 1000               | 6        | 1050              | 3        |
| 50 | 950               | 18       | 1000               | 6        | 1050              | 6        |
| 55 | 950               | 9        | 1000               | 6        | 1050              | 3        |
| 60 | 950               | 6        | 1000               | 6        | 1050              | 6        |
| 65 | 950               | 6        | 1000               | 3        | 1050              | 3        |
|    | 950               | 3        | 1000               | 2        | 1050              | 3        |
|    | 950               | 3        | 1000               | 2        | 1050              | 1        |
|    | 950               | 9        | 1050               | 3        | 1100              | 2        |
|    | 950               | 6        | 1050               | 3        | 1100              | 3        |
|    | 950               | 3        | 1050               | 4        | 1100              | 5        |

## Claims

1. A process of forming silica glass, which comprises:  
preparing a hydrolyzed solution of a metal alkoxide of formula  $M_x(OR)_x$  wherein M is a metal, R is an alkyl group and x has a value equivalent to the metal ion valence;  
5 forming a sol solution from the hydrolyzed solution;  
drying the sol solution to form a gel;  
drying the gel to a dry gel, and  
sintering the dry gel to form the silica glass, characterized in that the sol solution is formed by adding silica selected from fumed silica and silica gel to the hydrolyzed solution in an amount of 0.2 to 5 mols of silica per mol of metal alkoxide.
2. The process of claim 1, characterized in that the silica is formed by hydrolyzing  $SiCl_4$  with an oxy-hydrogen flame.
3. The process of claim 1, characterized in that said silica is derived from a sodium silicate solution.
4. The process of claim 1, characterized in that said silica is obtained by hydrolyzing a metal alkoxide with ammonia.
5. The process of claim 1, characterized in that it includes the step of dispersing the silica in the sol solution by ultrasonic vibration.
6. The process of claim 1, characterized in that it further includes the step of dispersing the silica in the sol solution by centrifugal separation.
7. The process of claims 1 to 6, characterized in that the metal alkoxide is ethyl silicate.
8. The process of claims 1-7, characterized in that the hydrolyzed metal alkoxide is ethyl silicate hydrolyzed with hydrochloric acid.
9. The process of claims 1-8, characterized in that it includes the step of adjusting the pH of the sol solution to between 3 and 6 by addition of a base.
- 20 10. The process of claims 1-9, characterized in that the pH of the sol solution is adjusted to between 4 to 4.5 by addition of a base.
11. The process of claim 9, characterized in that the base is any one of ammonia and an organic base.
12. The process of claim 11, characterized in that the ammonia is selected from the group of ammonia water, ammonia gas and an aqueous solution of ammonia.
- 30 13. The process of claim 11, characterized in that the organic base is selected from the group of triethylamine, an aqueous solution of pyridine, aniline or an aqueous aniline solution.
14. The process of claims 1-13, characterized in that it includes the step of drying the sol to a gel and the dry gel in a mold having a lid covering the mold and formed with apertures comprising less than 50% of the surface area of the lid.
- 35 15. The process of claim 9, characterized in that the sol is gelled in a mold having a lid covering the mold and formed with openings comprising less than 20% of the surface area of the lid.
16. The process of claim 1-15, characterized in that the gel is formed at temperatures between 5 to 60°C and the gel is dried to a dry gel at a drying temperature between 20 to 120°C.
- 40 17. The process of claim 16, characterized in that the gel is heated to the drying temperature at a rate less than 120°C per hour.
18. The process of claims 1-17, characterized in that the sintering of the dry gel includes the steps of (a) removing absorbed water; (b) removing carbon and (c) making the dry gel non-porous.
- 45 19. The process of claim 18, characterized in that it includes the step of removing absorbed water by heating the dry gel to a first selected temperature between 20 and 400°C at a heating rate of less than 400°C per hour and maintaining the dried gel at the selected temperature for at least one hour.
20. The process of claim 19, characterized in that it further includes the step of removing carbon by heating the dry gel to a second selected temperature between 400 and 1000°C at a heating rate of between 30 to 400°C per hour and maintaining the second selected temperature for a period of more than at least about 3 hours.
- 50 21. The process of claim 20, characterized in that it further includes the step of making the dry gel non-porous by heating the dry gel to a third selected temperature between 1000 to 1400°C at a heating rate of 30 to 400°C.
22. A process for forming silica glass at low temperature, which comprises:  
hydrolyzing a solution of ethyl silicate;  
55 casting the solution by pouring into a container of desired shape, sealing the container and permitting it to stand at room temperature to gel;  
replacing the cover of the container with a lid formed with apertures comprising between 0.5 to 20% of the surface area of the lid;  
60 drying the gel in the container to form a dry gel by heating to 60°C at a heating rate of 2°C per hour and drying for 7 days;  
heating the dry gel to 200°C at a heating rate of 60°C per hour and maintaining the dry gel at 200°C for one hour to remove absorbed water;  
heating the dry gel at a heating rate of 180°C per hour to 950°C and maintaining that temperature for 18 hours to remove carbon and ammonium chloride; and

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heating the dried gel to 1200°C at a heating rate of 180°C per hour and maintaining the temperature at 1200°C for 1.5 hour to yield the silica glass, characterized in that it comprises after the step of hydrolyzing and before the step of casting

adding fumed silica or silica gel powder to the solution in an amount from 0.4 to 5 mols of fumed silica or silica gel powder per mol of ethyl silicate;

adjusting the pH to between 4.0 to 4.5 by addition of ammonia to the solution:

### Patentansprüche

- 10 1. Ein Verfahren zur Herstellung von Quarzglas, wobei:  
Eine hydrolysierte Lösung eines Metallalkoxides der Formel  $Me(OR)_x$  bereitgestellt wird, wobei M für ein Metall, R für eine Alkylgruppe stehen und der Wert von "x" der Wertigkeit des Metallions entspricht; aus der hydrolysierten Lösung ein Sol (kolloidale Lösung) gebildet wird; das Sol zu einem Gel getrocknet wird; das Gel zu einem Trockengel getrocknet wird; und das Trockengel zu dem Quarzglas gesintert wird, dadurch gekennzeichnet, daß der hydrolysierten Lösung zur Bildung des Sol's Siliciumdioxid, nämlich pyrogene Kieselsäure und/oder Kieselgel in einem Anteil von 0,2 bis 5 Mol Siliciumdioxid pro Mol Metallalkoxid zugesetzt wird.
- 15 2. Das Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Kieselsäure durch Hydrolyse von Siliciumtetrachlorid ( $SiCl_4$ ) mit einer Sauerstoff-/Wasserstoff-Flamme gebildet wird.
- 20 3. Das Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Kieselgel aus einer Natriumsilikat-Lösung erhalten wird.
4. Das Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Kieselgel durch Hydrolyse eines Metallalkoxides mit Ammoniak erhalten wird.
- 25 5. Das Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Siliciumdioxid in dem Sol mittels Ultraschallschwingungen dispergiert wird.
6. Das Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Siliciumdioxid in dem Sol mittels Fliehkräfte-Schleudereinwirkung dispergiert wird.
7. Das Verfahren nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, daß Ethylsilikat als Metallalkoxid dient.
- 30 8. Das Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß als hydrolysiertes Metallalkoxid Ethylsilikat dient, das mit Salzsäure hydrolysiert worden ist.
9. Das Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß der pH-Wert des Sol's durch Zugabe einer Base auf einen Wert zwischen 3 bis 6 eingestellt wird.
- 35 10. Das Verfahren nach einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß der pH-Wert des Sol's durch Zugabe einer Base auf einen Wert von 4 bis 4,5 eingestellt wird.
11. Das Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß als Base Ammoniak oder irgendeine organische Base dient.
12. Das Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Ammoniak in Form von Ammoniakwasser, gasförmigem Ammoniak oder einer wässrigen Ammoniaklösung eingesetzt wird.
- 40 13. Das Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß als organische Base Triethylamin, eine wässrige Lösung von Pyridin und Anilin oder eine wässrige Anilin-Lösung eingesetzt wird.
14. Das Verfahren nach einem der Ansprüche 1 bis 13, dadurch gekennzeichnet, daß die Trocknung des Sol's zu einem Gel und die weitere Trocknung des Gels zu einem Trockengel in einer Form durchgeführt wird, die mit einem Deckel abgedeckt ist, der eine Öffnung aufweist, welche weniger als 50% der Deckeloberfläche ausmacht.
- 45 15. Das Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Trocknung des Sol's zu einem Gel in einer Form durchgeführt wird, die mit einem Deckel abgedeckt ist, der Öffnungen aufweist, welche weniger als 20% der Deckeloberfläche ausmachen.
16. Das Verfahren nach einem der Ansprüche 1 bis 15, dadurch gekennzeichnet, daß das Gel bei einer Temperatur zwischen 5 und 60°C gebildet wird, und das Gel bei einer Temperatur zwischen 20 und 120°C zu dem Trockengel getrocknet wird.
- 50 17. Das Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß die Erwärmung des Gels auf die Trocknungstemperatur mit einer Geschwindigkeit kleiner als 120°C pro Stunde erfolgt.
18. Das Verfahren nach einem der Ansprüche 1 bis 17, dadurch gekennzeichnet, daß die Sinterung des Trockengels nachstehende Verfahrensschritte einschließt:
  - (a) Entfernung von absorbiertem Wasser;
  - (b) Entfernung von Kohlenstoff; und
  - (c) Überführung des Trockengels in eine porenfreie Masse.
- 55 19. Das Verfahren nach Anspruch 18, dadurch gekennzeichnet, daß zur Entfernung von absorbiertem Wasser das Trockengel mit einer Aufwärmgeschwindigkeit kleiner als 400°C pro Stunde auf eine erste Temperatur zwischen 20 und 400°C erwärmt wird, und das Trockengel wenigstens eine Stunde lang bei dieser ersten Temperatur gehalten wird.
20. Das Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß zur Entfernung von Kohlenstoff das Trockengel mit einer Aufwärmgeschwindigkeit zwischen 30 und 400°C pro Stunde auf eine zweite
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Temperatur zwischen 400 und 1.000°C erwärmt wird, und länger als wenigstens ungefähr drei Stunden lang bei dieser zweiten Temperatur gehalten wird.

21. Das Verfahren nach Anspruch 20, dadurch gekennzeichnet, daß zur Überführung des Trockengels in eine porenfreie Masse das Trockengel mit einer Aufwärmgeschwindigkeit von 30 bis 400°C auf eine dritte

5 Temperatur zwischen 1.000 und 1.400°C erwärmt wird.

22. Ein Verfahren zur Herstellung von Quarzglas bei niedriger Temperatur, wobei:

Eine Ethylsilikat-Lösung hydrolysiert wird, diese Lösung in einen Behälter mit gewünschtem Innerraum gegossen wird, dieser Behälter verschlossen und daraufhin bei Raumtemperatur unbewegt gehalten wird, um das Gel zu bilden,

10 die Abdeckung auf dem Behälter durch einen Deckel mit Öffnungen ersetzt wird, welche 0,5 bis 20% der Deckelfläche ausmachen,

zur Bildung des Trockengels dieses Gel innerhalb des Behälters mit einer Aufwärmgeschwindigkeit von 2°C/h auf 60°C erwärmt und bei dieser Temperatur sieben Tage lang getrocknet wird,

das Trockengel mit einer Aufwärmgeschwindigkeit von 60°C/h auf 200°C erwärmt und eine Stunde lang

15 bei dieser Temperatur gehalten wird, um absorbiertes Wasser zu entfernen,

das Trockengel mit einer Aufwärmgeschwindigkeit von 180°C/h auf 950°C erwärmt und 18 Stunden lang bei dieser Temperatur gehalten wird, um Kohlenstoff und Ammoniumchlorid zu entfernen, und

das getrocknete Gel mit einer Aufwärmgeschwindigkeit von 180°C/h auf 1.200°C erwärmt und 1,5 Stunden lang bei dieser Temperatur gehalten wird, um Quarzglas zu erhalten, dadurch gekennzeichnet,

20 daß nach der Hydrolyse der Ausgangslösung und vor dem Eingießen in den Behälter der Lösung pyrogene Kieselsäure oder pulverförmiges Kieselgel in einem Anteil von 0,4 bis 5 Mol Siliciumdioxid pro Mol Ethylsilikat zugesetzt wird, und durch Zugabe von Ammoniak zu der Lösung deren pH-Wert auf einen Wert zwischen 4,0 und 4,5 eingestellt wird.

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### Revendications

1. Procédé de formation de verre à base de silice qui consiste:

à préparer une solution hydrolysée d'un alcoolate métallique de formule  $M_x(OR)_y$ , dans laquelle M est

30 un métal, R est un groupe alcoyle et x a une valeur équivalente à la valence de l'ion métallique;

à former une solution de sol à partir de la solution hydrolysée;

à sécher la solution de sol pour former un gel;

à sécher le gel en un gel sec, et

à préfondre le gel sec pour former le verre à base de silice,

35 caractérisé en ce qu'il consiste à former la solution de sol en ajoutant de la silice choisie parmi la silice fumée et un gel de silice à la solution hydrolysée en une quantité de 0,2 à 5 moles de silice par mole d'alcoolate métallique.

2. Procédé suivant la revendication 1, caractérisé en ce qu'il consiste à former la silice en hydrolysant du  $SiCl_4$  au chalumeau oxydrique.

40 3. Procédé suivant la revendication 1, caractérisé en ce que la silice provient d'une solution de silicate de sodium.

4. Procédé suivant la revendication 1, caractérisé en ce qu'il consiste à obtenir la silice en hydrolysant un alcoolate métallique par de l'ammoniaque.

5. Procédé suivant la revendication 1, caractérisé en ce qu'il comprend le stade de dispersion de la silice dans la solution de sol par vibrations ultrasonores.

6. Procédé suivant la revendication 1, caractérisé en ce qu'il comprend, en outre, le stade de dispersion de la silice dans la solution de sol par séparation centrifuge.

7. Procédé suivant les revendications 1 à 6, caractérisé en ce que l'alcoolate de métal est du silicate d'éthyle.

50 8. Procédé suivant les revendications 1 à 7, caractérisé en ce que l'alcoolate de métal hydrolysé est du silicate d'éthyle hydrolysé par de l'acide chlorhydrique.

9. Procédé suivant les revendications 1 à 8, caractérisé en ce qu'il comprend le stade d'ajustement du pH de la solution de sol entre 3 et 6 par addition d'une base.

10. Procédé suivant les revendications 1 à 9, caractérisé en ce qu'il consiste à ajuster le pH de la solution de sol entre 4 et 4,5 par addition d'une base.

55 11. Procédé suivant la revendication 9, caractérisé en ce que la base est un produit ammoniaqué ou une base organique.

12. Procédé suivant la revendication 11, caractérisé en ce qu'il consiste à choisir le produit ammoniaqué parmi l'eau ammoniacale, l'ammoniac gazeux et une solution aqueuse d'ammoniaque.

60 13. Procédé suivant la revendication 11, caractérisé en ce qu'il consiste à choisir la base organique parmi la triéthylamine, une solution aqueuse de pyridine, l'aniline ou une solution aqueuse d'aniline.

14. Procédé suivant les revendications 1 à 13, caractérisé en ce qu'il comprend le stade de séchage du sol en un gel et en le gel sec dans un moule ayant un couvercle recouvrant le moule et muni d'ouvertures représentant moins de 50% de la surface du couvercle.

65 15. Procédé suivant la revendication 9, caractérisé en ce qu'il consiste à gélifier le sol dans un moule

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ayant un couvercle recouvrant le moule et muni d'ouvertures représentant moins de 20% de la surface du couvercle.

16. Procédé suivant les revendications 1 à 15, caractérisé en ce qu'il consiste à former le gel à des températures comprises entre 5 et 60°C et à sécher le gel en un gel sec à une température de séchage comprise entre 20 et 120°C.

17. Procédé suivant la revendication 16, caractérisé en ce qu'il consiste à porter le gel à la température de séchage à une vitesse inférieure à 120°C à l'heure.

18. Procédé suivant les revendications 1 à 17, caractérisé en ce que la préfusion du gel sec comporte les stades qui consistent à (a) éliminer l'eau absorbée; (b) éliminer le carbone et (c) rendre le gel sec non poreux.

19. Procédé suivant la revendication 18, caractérisé en ce qu'il comprend le stade d'élimination de l'eau absorbée en portant le gel sec à une première température choisie, comprise entre 20 et 400°C, à une vitesse de chauffage inférieure à 400°C à l'heure et de maintien du gel séché à la température choisie pendant au moins une heure.

20. Procédé suivant la revendication 19, caractérisé en ce qu'il comprend, en outre, le stade d'élimination du carbone en portant le gel sec à une deuxième température choisie, comprise entre 400 et 1000°C à une vitesse de chauffage comprise entre 30 et 400°C à l'heure, et de maintien de la deuxième température choisie pendant une durée supérieure à au moins 3 heures environ.

21. Procédé suivant la revendication 1, caractérisé en ce qu'il consiste, en outre, à rendre le gel sec non poreux en portant le gel sec à une troisième température choisie, comprise entre 1000 et 1400°C, à une vitesse de chauffage de 30 à 400°C.

22. Procédé de formation d'un verre à base de silice à basse température, qui consiste:  
à hydrolyser une solution de silicate d'éthyle;  
à couler la solution en la versant dans un récipient de forme souhaitée, à sceller le récipient et à l'abandonner à la température ambiante pour qu'elle se prenne en gel;  
à remplacer le couvercle du récipient par un couvercle muni d'ouvertures représentant entre 0,5 et 20% de la surface du couvercle;  
à sécher le gel dans le récipient pour former un gel sec en le portant à 60°C à une vitesse de chauffage de 2°C à l'heure et en le séchant pendant 7 jours;  
à porter le gel sec à 200°C à une vitesse de chauffage de 60°C à l'heure et en maintenant le gel sec à 200°C pendant une heure pour éliminer l'eau absorbée;  
à porter le gel sec à 950°C à une vitesse de chauffage de 180°C à l'heure et à maintenir cette température pendant 18 heures pour éliminer le carbone et le chlorure d'ammonium; et  
à porter le gel séché à 1200°C à une vitesse de chauffage de 180°C à l'heure et à maintenir la température à 1200°C pendant 1,5 heure pour obtenir le verre à base de silice, caractérisé en ce qu'il consiste, après le stade d'hydrolyse et avant le stade de coulée,  
à ajouter de la silice fumée ou de la poudre de gel de silice à la solution en une quantité de 0,4 à 5 moles de silice fumée ou de poudre de gel de silice par mole de silicate d'éthyle;  
à ajuster le pH autre 4,0 et 4,5 par addition d'un produit ammoniaqué à la solution.

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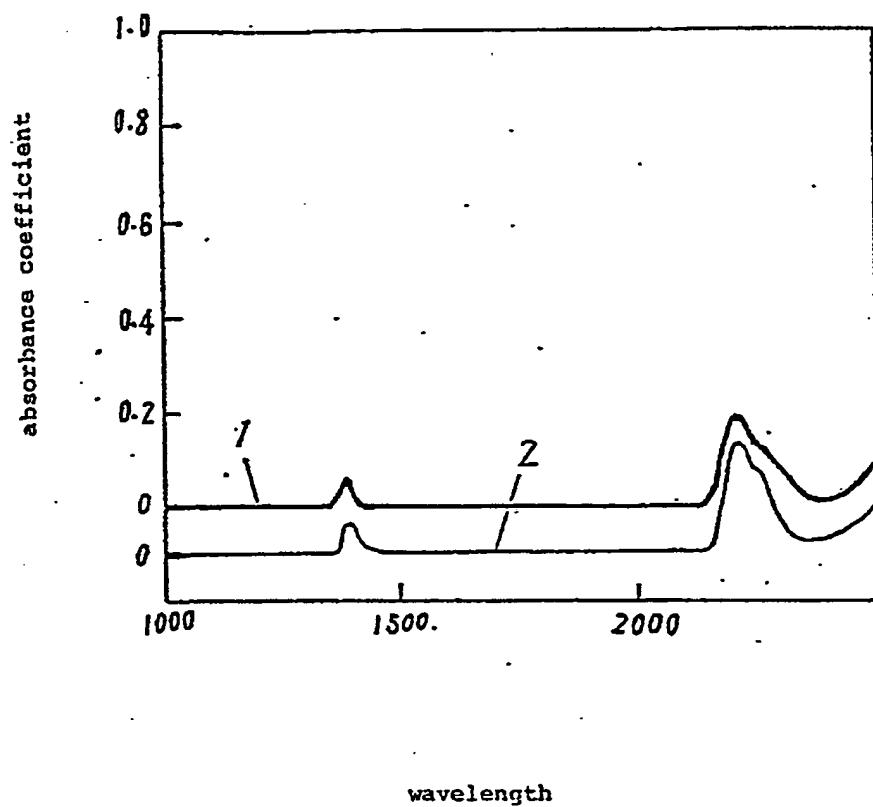
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